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# AN INVESTIGATION OF THE RADIOLYTICALLY ENHANCED OXIDATION OF CARBON-14 PARTICULATE

*Report No 88-160-K*

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## *ABSTRACT*

The injection of oxygen into the nitrogen-filled gas annulus systems at Pickering NGS has been proposed as a method of carbon-14 decontamination prior to retubing. The thermal oxidation of carbon-14 particulate produced in a nitrogen gas annulus system has already been investigated at Chemical Research but until the present study no data has been available on the influence of radiation on carbon-14 gasification rates. Samples of particulate carbon-14 have therefore been subjected to radiolysis in air in a high-flux research reactor for periods up to four days. Carbon-14 oxidation rates of 1-2%/day have been observed for radiation exposure rates of ~300 MR/day. This corresponds to a carbon-14 oxidation rate about 100 times the rate expected by thermal oxidation alone. It was also observed that non-active carbon-12-hydrocarbons, invariably present in gas annulus deposits, oxidize more readily than carbon-14 and it is postulated that this limits the formation of $NO_2$, the deleterious air radiolysis by-product.



| job | file | date | report no. |
|---|---|---|---|
| 33-259-562 | 833.74 | August 4, 1988 | 88-160-K |

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# AN INVESTIGATION OF THE RADIOLYTICALLY ENHANCED OXIDATION OF CARBON-14 PARTICULATE

It is now well established that a carbon-14-rich solid accumulates in reactors operated with nitrogen-filled gas annulus systems/1/. It has been proposed that carbon-14 atoms, produced by the $^{14}N(n,p)^{14}C$ reaction, undergo reactions with other species in the annulus gas to form $H^{14}CN$ type intermediates which subsequently deposit on reactor surfaces as an intractable polymeric material/2/.

Investigations carried out at Chemical Research have shown that the $^{14}C$-polymer produced in Pickering NGS Unit 2 prior to retubing is quite inert, being only slightly soluble in common solvents, but is slowly oxidized by air even at room temperatures. Because the oxidation products are gaseous $^{14}CO$ or $^{14}CO_2$, exposure of the $^{14}C$-polymeric material to air or oxygen represents a potential method for the decontamination of a gas annulus system. However, before such an oxidative decontamination process may be utilized at Pickering NGS, it is desirable to have experimental data on the rates of oxidation of the $^{14}C$-polymer under conditions which duplicate typical reactor environments.

Laboratory measurements made to date indicate that the oxidation of $^{14}C$-deposits occurs relatively slowly at temperatures appropriate to a gas annulus system under reactor heating (~165°C) but data are not available on the influence of radiation on carbon-14 gasification rates/3/.

This report documents the results of radiolytic oxidation experiments carried out on samples of $^{14}C$-rich particulate material from Pickering Unit 2 and shows that enhanced oxidation does indeed occur in the presence of radiation fields. The extent of some important associated reactions such as the formation of nitrogen oxides ($N_2O$, $NO_2$ and NO) is also considered.

## 1. ANALYTICAL PROCEDURES

All irradiation experiments were carried out with carbon-14 particulate samples sealed in custom-made quartz ampoules. The ampoules were made at the University of Toronto

glassblowing shop with the following specifications: Height - 3.8 cm; Diameter - 1.8 cm, (Approximate volume - 10 $cm^3$). Two side arms were attached to one end of each ampoule, one for sample introduction and the other, with an internal break-seal, for the extraction of the gaseous contents of the ampoule after an irradiation.

Samples of particulate carbon-14 were collected by rubbing 1-2 cm lengths of iron or aluminum wire on a calandria tube protective sleeve or "tophat" which had been inserted into Pickering Unit 2 during retubing operations/2/. Only very small amounts (~10μg) of particulate material could be transferred to an ampoule in this way. However, because of the very high specific activity of the carbon-14 particulate, the activity transferred (~10μCi) was quite sufficient to make subsequent radiometric measurements with good precision.

To facilitate the gas filling and sealing of the ampoules laboratory air at close to atmospheric pressure was used in all experiments. The sealed ampoules were subjected to gamma-ray or neutron irradiations at the McMaster University Reactor Facility as detailed in the results presented below. After an irradiation the ampoule was returned to Chemical Research for analysis of the radiolysis products.

Detailed analytical procedures differed somewhat from sample to sample but the following scheme was generally adhered to. The irradiated ampoule was connected with a short length of tubing to a 5 cm infrared cell, employing KBr windows, and the cell and connecting tube evacuated. The internal break-seal on the ampoule was then broken with a magnetically activated plunger and the gaseous contents of the ampoule allowed to fill the combined volume of the ampoule and the infrared cell (~50 $cm^3$). Spectra were recorded in the wave number range from 4000-500 $cm^{-1}$ with a resolution of 0.5 $cm^{-1}$ on a Mattson Cygnus 25 FTIR (Fourier Transform Infrared) spectrometer (see Appendix). After completion of spectral analysis the ampoule and infrared cell were incorporated into a simple gas-sampling train. Air was drawn through the train by a metal bellows pump and the purged $^{14}CO$ and $^{14}CO_2$ trapped and assayed by liquid scintillation counting, (LSC). ($^{14}CO$ trapping was accomplished by oxidation to $^{14}CO_2$ with hopcalite heated to 350°C). The solid carbon-14 remaining in the irradiated ampoule was determined by vigorous heating of the purged ampoule (~1000°C) accompanied by trapping and LSC of liberated $^{14}CO_2$.

## 2. RESULTS

The results of the carbon-14 oxidation experiments carried out in this investigation are presented in Table 2.1.

## 3. DISCUSSION

The data reported in Table 2.1 show that in the absence of radiation fields the carbon-14 particulate oxidation rate at 20°C is extremely low, namely 0.0045%/day. The main oxidation product is $^{14}CO_2$ with only a trace of $^{14}CO$ (4% relative to $^{14}CO_2$).

Exposure of the carbon-14 particulate to a gamma-ray field of 0.66 MR/hour increases the oxidation rate by a factor of about 6. However, it may be shown that (see Note 2) about half of this increase is due to the heating effect of the gamma rays. In fact, the same carbon-14 oxidation rate could be achieved by heating the material to about 40°C. By comparison,

TABLE 2.1: Results of Experiments on the Radiolytically Enhanced Oxidation of Carbon-14 Particulate

| Experiment Number | Initial Sample Activity (nCi) | Irradiation Conditions: Cover Gas | Irradiation Conditions: Temp (°C) | Irradiation Conditions: Time (Days) | Type of Irradiation and Exposure Rate[1] | Total Radiation Exposure[1] (MR) | Post Irradiation Activity in Cover Gas: $^{14}CO$ (nCi) | Post Irradiation Activity in Cover Gas: $^{14}CO_2$ (nCi) | Post Irradiation Activity in Cover Gas: $\frac{^{14}CO}{^{14}CO_2}$ | Carbon-14 Oxidation Rate[2] (%/Day) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 3360 | Air (1 Atm) | 20 | 6.3 | No Radiation | 0 | 0.040 | 0.922 | 0.04 | 0.0045 (±0.0004) |
| 2 | 4510 | Air (1 Atm) | ~30 | 6.3 | γ-Ray; 0.66 MR/hour | 100 | 0.400 | 6.602 | 0.06 | 0.025 (±0.001) |
| 3 | 0 | Air (~0.5 Atm) | ~40 | 3.7 | Mixed Neutron + γ-Ray $6.3 \times 10^{12}$ n $cm^2$ $s^{-1}$ | ~1000 | 13.2 | 4.6 | 2.87 | - |
| 4 | 14250 | Air (~0.75 Atm) | ~40 | 3.7 | Mixed Neutron & γ-Ray $6.3 \times 10^{12}$ n $cm^2$ $s^{-1}$ | ~1000 | 364 | 1177 | 0.31 | 2.64 (±0.04) |
| 5 | 28110 | Air (~0.75 Atm) | ~40 | 3.7 | Mixed Neutron + γ-Ray $6.3 \times 10^{12}$ n $cm^2$ $s^{-1}$ | ~1000 | 43 | 1040 | 0.04 | 1.00 (±0.02) |

Notes: 1. Dosimetry )
2. Carbon-14 Oxidation Rates ) See Following page
3. Other matters pertaining to these results and FTIR data on the post-irradiation composition of the cover gases are discussed in Section 3.0.

(Cont'd) TABLE 2.1: Results of Experiments on the Radiolytically Enhanced Oxidation of Carbon-14 Particulate

Notes:

1. Dosimetry

The exposure rate for the sample irradiated in the gamma-cell was measured by an ionization chamber and is considered to be accurate to with ±5%. For gamma-ray irradiations of air an absorbed dose of D rad is numerically quite similar to an exposure of X roentgen (symbol, R) or more precisely

$$D = 0.873 \text{ X } \frac{\text{rad}}{\text{R}} .$$

In the case of reactor irradiations both the exposure and absorbed dose are difficult to specify precisely due to the well documented problems associated with neutron dosimetry/4/.

It is known that energy is dissipated in a sample during reactor irradiation by several mechanisms: neutron scattering, primary (fission) and secondary (capture) gamma-ray absorption and the scattering of particles produced by nuclear reactions. W. Primak and L. Fuchs have shown that, for small samples of air irradiated by a neutron flux, approximately half of the absorbed dose arises from the kinetic energy of the proton and recoiling $^{14}C$ nucleus released by the $^{14}N(n,p)^{14}C$ reaction while the other half is contributed by the co-existing gamma-radiation field/5/. In the present investigations samples were exposed to a measured thermal neutron flux of $6.3 \times 10^{12}$ n $cm^{-2}s^{-1}$ for 88 hours. If the computational approach given in reference 5 is followed, a combined gamma-ray and neutron dose of about 1000 M rad may be estimated for the integrated flux of $2 \times 10^{18}$ neutrons $cm^{-1}$. However, the error in this estimate may be as large as ±50%.

2. Carbon-14 Oxidation Rates

The heating effects inherent in radiolysis experiments must be borne in mind in assessing the oxidation rates reported in Table 2.1. Thus a knowledge of the average temperature attained by a sample during an irradiation is required to separate an observed reaction rate into a purely thermal contribution due to radiolytic effects.

The temperatures reported in Table 2.1 are values quoted by the McMaster Reactor Facility personnel as typical for the experimental conditions employed and are probably accurate to only ±2 °C. Nonetheless, these temperatures provide at least an order of magnitude estimate of the radiolytic enhancement of a carbon-14 oxidation rate.

The data previously reported in/3/ shows that the carbon-14 thermal oxidation rate increases by a factor of about 1.7 for a 10° C increase in temperature. (At least over the temperature range 20° - 50° C). Thus it may be calculated from Table 2.1 that the rate enhancement factors attributable to radiolytic effects alone are 3.3 for gamma-radiolysis and 80 for mixed gamma-ray and neutron radiolysis.

reactor irradiation of the carbon-14 particulate at exposure rates equivalent to ~10 MR/hour results in an average oxidation rate enchancement about 80 times greater than that from heating effects alone. However, because reactor irradiation involves exposure not only to neutrons but also to gamma rays, with each contributing about 50% of the absorbed dose (see Note 1), it may be concluded that neutrons and gamma rays are approximately equally effective in promoting the oxidation of carbon-14 particulate. A similar conclusion was reached by K. Kosiba and G. Dienes in their investigation of the radiolytically enhanced oxidation of graphite/6/.

It is clear, therefore, that absorbed doses less than about 100 Mrad produce only marginal effects on carbon-14 particulate oxidation rates. On the other hand, doses of 1000 Mrad or more produce substantial rate enhancement effects. The reactor irradiation experiments Nos 3-5 involve radiation doses of this order of magnitude and will now be considered in detail.

### 3.1 Experiment No 3:
### The Reactor Irradiation of Air in the Absence of Initial Carbon-14

It was considered appropriate to carry out an irradiation experiment with no carbon-14 particulate initially present in the ampoule to investigate the quantity and chemical speciation of the carbon-14 produced by neutron irradiation of air alone.

As reported in Table 2.1, 13.2 nCi of $^{14}CO$ and 4.6 nCi of $^{14}CO_2$ were found in the gas purged from the ampoule after the irradiation. This indicates that $^{14}CO$, not $^{14}CO_2$, is the major carbon-14 containing gas-phase species produced by the neutron irradiation of air in agreement with the observations of M. Pandow et al/7/. However, when the purged ampoule was heated in air to > 500°C an additional 0.4 nCi of $^{14}CO$ and 3.0 nCi of $^{14}CO_2$ was released, an amount equal to about 16% of the total carbon-14 found in the ampoule.

H. Ache and A. Wolf have shown that the primary products stemming from "hot" carbon atom reactions in mixtures of oxygen and nitrogen are CO and CN with oxygen being about nine times more reactive than nitrogen/8/. On this basis radiolysis of air should produce $^{14}CO$ and $^{14}CN$ in the ratio 2.25:1. However, it may be anticipated that prolonged irradiation of these species will result in the formation of carbon-14-suboxide, and carbon-14 cyanide polymers/8,9/. These polymers deposit on the walls of the irradiation vessel and yield $^{14}CO$, $^{14}CO_2$ and $N_2$ on subsequent heating in air.

The 16% carbon-14 deposition observed in the present investigation is mainly a result of the high radiation exposure ($>10^{18}$ n/cm$^{2)}$ given to the sample in a non-flowing system, an experimental regime permitting extensive secondary radiolytic reactions to occur.

The composition of the air in the ampoule after the reactor irradiation was investigated by FTIR (Fourier Transform Infrared) spectroscopy. This technique has previously not been widely used at Chemical Research for gas analysis and an extensive programme of calibrations was therefore undertaken to convert the measured spectral absorbances into concentration data. (The resulting calibration factors are estimated to be accurate to better than ±10%, however, because of uncertainties in the sample pressures, the inter-sample errors in the reported concentrations may be as high as ±25%).

The principal species detected in the irradiated air from experiment No 3 were $^{12}CO_2$, $^{12}CO$, $NO_2$, $N_2O$, and NO. The measured concentrations of these gases are given in Table 3.1.

TABLE 3.1

Concentrations of Gases Formed by the Radiolysis of Air
(Experiment No 3)

| Gas Conc | $^{12}CO_2$ | $^{12}CO$ | $NO_2$ | $N_2O$ | NO |
|---|---|---|---|---|---|
| ppm (V/V) | 900 | 200 | 800 | 4500 | 400 |

The radioactive gas $^{14}CO_2$ was not detected in the FTIR spectrum of this sample due to its low concentration. It may be calculated that the 4.6 nCi of $^{14}CO_2$ found in the ampoule by liquid scintillation counting, (see Table 2.1), is equivalent to about 0.2 ppm (V/V); this is well below the estimated $^{14}CO_2$ detection limit for FTIR analysis as performed at Chemical Research of about 5 ppm (V/V).

The results presented in Table 3.1 show that, as expected, substantial production of nitrogen oxides occurs during the radiolysis of air. Nitrous oxide, $N_2O$, was found to be the major product with an effective G-value (Number of molecules produced per 100 eV of absorbed energy) of about 2.

Unfortunately very limited data have been published in the open literature on the radiolysis of air/10/. The most detailed study that is readily available appears to be that of P. Harteck and S. Dondes/11/ who reported data on the production of $NO_2$ and $N_2O$ for different $N_2$ and $O_2$ mixtures over a range of radiation doses. These authors' results show that both $NO_2$ and $N_2O$ may build up to concentrations in excess of 1% from radiation doses in excess of $10^9$ R but the $NO_2/N_2O$ ratio appears to be strongly dependent on factors such as the radiation dose, the gas pressure and the presence of minor species such as $CO_2$.

## 3.2 Experiments Nos 4 and 5: The Reactor Irradiation of Air in the Presence of Initial Carbon-14 Particulate

Two separate experiments were carried out to measure the oxidation rate of carbon-14 particulate in a radiolytic environment. In these experiments, referred to as Nos 4 and 5, two samples containing 14.25 μCi and 28.11 μCi of solid carbon-14 from a Pickering Unit 2 (P2) "tophat" were sealed in quartz ampoules and exposed to ~1000 MR of reactor radiation.

The results of FTIR analysis of the gases extracted from the ampoules after the irradiations are reported in Table 3.2.

TABLE 3.2

Concentrations of Gases Formed by the Reactor Irradiation of Carbon-14 Particulate in Air (Experiments Nos 4 and 5)

| | Gas Conc | $^{12}CO_2$ | $^{12}CO$ | $NO_2$ | $N_2O$ | NO |
|---|---|---|---|---|---|---|
| Expt No 4 | ppm (V/V) | 5800 | 1200 | 10700 | 17600 | Not Analyzed |
| Expt No 5 | ppm (V/V) | 7400 | 430 | <100 | 3300 | <100 |

The principal species detected in both experiments after the irradiations were $^{12}CO_2$, $^{12}CO$ and $N_2O$; substantial amounts of $NO_2$ were also observed in experiment No 4 but not in experiment No 5.

The radioactive species $^{14}CO_2$ was detected by FTIR analysis only in the case of experiment No 5. (The IR spectrum below 2000 $cm^{-1}$ was not recorded for experiment No 4 thereby precluding the detection of $^{14}CO_2$; see Appendix). The measured concentration of $^{14}CO_2$ in experiment No 5 of about 55 ppm (V/V) was converted to an activity by comparison of the sample IR spectrum with the spectrum of a $^{14}CO_2$ standard of known activity. The activity determined in this way was 1.3 ±0.3 μCi in reasonable agreement with the value of 1.04 μCi measured by trapping and counting of the active contents of the ampoule subsequent to IR analysis (see Table 2.1).

The observation of far more $^{12}CO_2$ (6000-8000 ppm) than $^{14}CO_2$ (50-60 ppm) in the radiolytic oxidation products of P2 carbon-14 samples raises the question of the $^{12}C/^{14}C$ ratio to be expected for these experiments. It is known from previous measurements/2/ that the P2 particulate material contains up to four times as much carbon-14 as carbon-12 (i.e. $^{12}C/^{14}C = 0.25$). Hence it may be estimated that the following amounts of solid carbon-12 and carbon-14 were sealed in the ampoules for the irradiation experiments:

| | Experiment No 4 | Experiment No 5 |
|---|---|---|
| μg $^{12}C$ | 4 | 7 |
| μg $^{14}C$ | 14 | 28 |

It follows that in the absence of any carbon isotope effects, approximately four times more $^{14}CO_2$ than $^{12}CO_2$ should be found in the product gases. The contrary observation of a far higher concentration of $^{12}CO_2$ than $^{14}CO_2$ in the radiolytic oxidation products of experiment No 4 was therefore quite unexpected and led to an attempt to analyze the gases initially sealed in the ampoule of experiment No 5 to identify the source of the excess carbon-12.

It proved possible to measure in-situ the $^{12}CO_2$ content of the air sealed in the quartz ampoule by FTIR analysis (The 2349 $cm^{-1}$ absorption band of $^{12}CO_2$ was used which lies just above the 2000 $cm^{-1}$ cut-off of quartz). In this way it was determined that 4000 ± 1000 ppm (V/V) of $^{12}CO_2$ was already present in the ampoule of experiment No 5 prior to irradiation. However, because 7400 ppm (V/V) of $^{12}CO_2$ was found in the post irradiation ampoule of experiment No 5 (see Table 3.2), an amount equivalent to at least 2400 ppm of $^{12}CO_2$ was evidently liberated from the P2 sample by radiolytic oxidation. This concentration of $^{12}CO_2$ converts to about 13μg of carbon-12 compared to the 7 μg previously calculated to be in the sample.

An explanation of the larger than expected production of $^{12}CO_2$ in these experiments may be found in the common occurrence of carbon-12 in the environment. Almost any material when probed by a surface sensitive analytical technique reveals superficial contamination by carbonaceous species. Surface contaminations up to 1 $\mu g/cm^2$ may result from carbon contamination of this type. If, for example, the inside of a $10cm^3$ quartz ampoule is covered with a layer of carbonaceous material only ten atoms thick, about 6 μg of carbon-12 are effectively added to any sample sealed in this ampoule. Furthermore, because the P2 carbon-14 was found to undergo radiolytic oxidation at the relatively slow rate of 1-2%/day, it must also be concluded that the carbon-12 species co-irradiated in the present study are oxidized far more rapidly than their carbon-14 counterparts.

It has, in fact, already been proposed that the carbon-12 species in the P2 "tophat" material are mainly simple aliphatic hydrocarbons while the carbon-14 occurs as a mixture of complex nitrogen heterocyclic polymers/2/. It is therefore very probable that the former species oxidize more rapidly than the latter and hence the presence of any amount of $^{12}C$-hydrocarbon in a P2 sample necessarily strongly inhibits gassification of the carbon-14.

The early investigations on the radiation induced reactions of nitrogen-oxygen mixtures carried out by A.R. Jones at the Oak Ridge National Laboratory are very relevant in this context/12/. This author reported that the addition of a nonvolatile hydrocarbon grease to an irradiation cell "effectively prevented the formation of nitrogen oxides **other than nitrous oxide**." It follows from this result that the smaller amounts of carbon-12 containing hydrocarbons irradiated in experiment No 4 compared with experiment No 5 should result in the lower production of $NO_2$ in the latter case; this prediction is dramatically supported by the measured $NO_2$ concentrations reported in Table 3.2.

3.3 Oxygen Injection Studies at Pickering NGS

In concluding this report mention should be made of the ramifications of the present results on the oxygen injection studies being undertaken at Pickering NGS. In one such test, completed on May 1, 1988, 50 litres of oxygen were added to the nitrogen annulus gas system of Unit 4. Gas samples (300 $cm^3$ at about atmospheric pressure) were collected at regular intervals after the injection and analyzed by gas chromatography (GC). The complete results of these measurements have been reported elsewhere/13/. The sample containing the highest concentration of $^{14}CO_2$, designated sample 1C taken 19:20 hrs, April 29, was also investigated by FTIR analysis at Chemical Research and is discussed below.

The gases detected by FTIR analysis of sample 1C were $^{14}CO_2$, $^{12}CO_2$ and $N_2O$. (Other nitrogen oxides, and in particular NO and $NO_2$, were not detected by either FITR or GC analysis.) The measured concentrations of the gases identified in sample 1C are reported in Table 3.3. (Precise quantification of $^{12}CO_2$ by FTIR was not attempted due to interference by trace atmospheric $^{12}CO_2$ in the purged instrument compartment.)

TABLE 3.3

Concentrations of Gases Found in Sample 1C Taken after the Injection of 50 L of $O_2$ into the Pickering Unit 4 $N_2$ Annulus

| Analytical Technique | $^{14}CO_2$ (μCi/L) | $^{12}CO_2$ ppm $(\frac{V}{V})$ | $N_2O$ ppm $(\frac{V}{V})$ | $NO_2$ ppm $(\frac{V}{V})$ |
|---|---|---|---|---|
| FTIR | 40 ± 10 | ~80 | 150 ± 40 | <100 |
| GC | 30 ± 3 | 29 ± 3 | 130 ± 10 | <5 |

Inspection of the data in Table 3.3 shows that the concentrations of gases measured by FTIR are uniformly higher than those measured by GC. This is undoubtedly due to the uncertainty in the sample pressure in the FTIR cell which was assumed to be one atmosphere but was evidently somewhat higher.

Regardless of the small discrepancies between the FTIR and GC data two major conclusions may be drawn from the analysis of sample 1C:

(i) If the $^{14}CO_2$ and $^{12}CO_2$ concentrations are placed on an equivalent basis, (1μCi/L $^{14}CO_2$ ~ 0.4 ppm (V/V) ), the concentration of $^{12}CO_2$ is higher than the concentration of $^{14}CO_2$.

(ii) Nitrous oxide, $N_2O$, is the only significant oxide of nitrogen occurring in this sample.

These conclusions once again serve to emphasize the importance of carbon-12 in the radiolytic oxidation of carbon-14 solids in nitrogen gas annulus systems. As shown in Section 3.2 of this report there is good evidence that the carbon-12 occurring in the Pickering gas annulus system deposits is chemically quite different from the carbon-14 species with which it is associated. It is further proposed that the carbon-12 occurs mainly as aliphatic hydrocarbons, perhaps from oil or grease residues, and is more readily oxidized than the highly polymerized and conjugated carbon-14. This being the case, for small injections to a Pickering annulus, much of the available oxygen would be consumed in oxidizing carbon-12 deposits to $^{12}CO_2$ and $H_2O$. Only after the carbon-12 is depleted could $^{14}CO_2$ production exceed that of $^{12}CO_2$.

This picture also explains the absence of $NO_2$ in sample 1C. Thus it appears that $N_2O$ is always produced in the radiolysis of nitrogen-oxygen mixtures by the reaction of $N_2$ ($A^3\Sigma_u^+$) with $O_2$. By comparison $NO_2$ is formed mainly from oxygen atoms, probably via NO, and these atoms are also efficiently scavenged by carbonaceous species. Hence, again for small oxygen injections, $NO_2$ is only likely to appear after the depletion of carbon-12.

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## APPENDIX

## FTIR SPECTRUM ANALYSIS OF $^{14}CO_2$

FTIR Spectroscopy has proved to be very useful not only for the analysis of gases produced in the present studies of the radiolytic oxidation of carbon-14, but also for the analysis of Pickering NGS gas-annulus samples. Among the gases readily analyzed with the equipment available at Chemical Research, namely a Mattson Cygnus 25 spectrometer, are $CO_2$, CO, $NO_2$, $N_2O$ and NO. However, radioactive gases such as $^{14}CO_2$ and $^{14}CO$ are also detectable by the technique as are the various isotopically substituted water species such as $D_2O$ and HDO.

In applying FTIR analysis to gas mixtures, it is important to carefully select absorption features which are free from interferences. The Mattson instrument as it is currently configured at Chemical Research covers the spectral range from 2.5 μm to 20 μm corresponding to the wave number range of 4000 $cm^{-1}$ to 500 $cm^{-1}$. Within this range simple molecules exhibit most of the absorption bands due to their fundamental vibrations but many weaker combination and overtone bands may also be observed. Thus even for the "simple" triatomic molecule $CO_2$, Herzberg/1/ lists sixteen bands in the spectral range from 4000-500 $cm^{-1}$ in addition to the fundamental bands at 667.3 $cm^{-1}$ and 2349.3 $cm^{-1}$.

Water presents a special problem in the analysis of gases by FTIR. Firstly, it is very difficult to remove the last traces of water from an IR cell and secondly water has very intense and complex vibrational absorption bands in the regions 3900-3600 $cm^{-1}$ and 1800-1400 $cm^{-1}$ as well as a multitude of pure rotational absorption lines below 720 $cm^{-1}$. Fortunately excellent tabulations of the positions and relative intensities of these lines have been published/2/.

The acquisition of reference spectra of gases suspected of being present in a sample is without doubt the best approach to the identification of potential spectral interferences. A good illustration of this is provided by Figures 1-3. Figure 1 shows the spectrum of a $^{14}CO_2$ standard in the spectral region from 2450 $cm^{-1}$ to 2050 $cm^{-1}$. The very strong transition centered at 2226.0 $cm^{-1}$ is the $\upsilon_3$ transition of $^{14}CO_2$ with the rotational fine structure of the P and R branches well resolved/3/. The weaker transition centered at 2349.4 $cm^{-1}$ is the $\upsilon_3$ transition of $^{12}CO_2$ caused by the contamination of the carbon-14 standard by non-active carbon dioxide/4/. The relative peak intensities in Figure 1 show that the $^{14}CO_2$ and $^{12}CO_2$ ratio is about 3:1.

Figure 2 is the spectrum of the P4 gas annulus sample 1C recorded over the same wavenumber range as Figure 1. At first sight it might be concluded that sample 1C contains $^{14}CO_2$ and $^{12}CO_2$ in the approximate ratio of 1:2. However, inspection of the spectrum of an $N_2O$ standard, Figure 3, reveals the remarkably close coincidence of the $\upsilon_3$ band of this molecule at 2223.5 $cm^{-1}$ with $\upsilon_3$ of $^{14}CO_2$ at 2226.0 $cm^{-1}$/5/. Only by moving to an entirely different region of the spectrum, where other vibrational bands of these molecules occur, may this interference be resolved. Thus Figure 4 shows the spectrum of the same P4 gas annulus sample in the spectral range 700-500 $cm^{-1}$. The strong absorption at 667.3 $cm^{-1}$ is the Q branch of the $\upsilon_2$ bending vibration of $^{12}CO_2$/16/. The weaker features

at 632.2 $cm^{-1}$ and 588.8 $cm^{-1}$ are the equivalent absorptions due to $^{14}CO_2$ /3/ and $N_2O$ /7/, respectively, confirming that both these species are indeed present in this sample. Figures 5 and 6 are the spectra of $^{14}CO_2$ and $N_2O$ standard in this spectral range.

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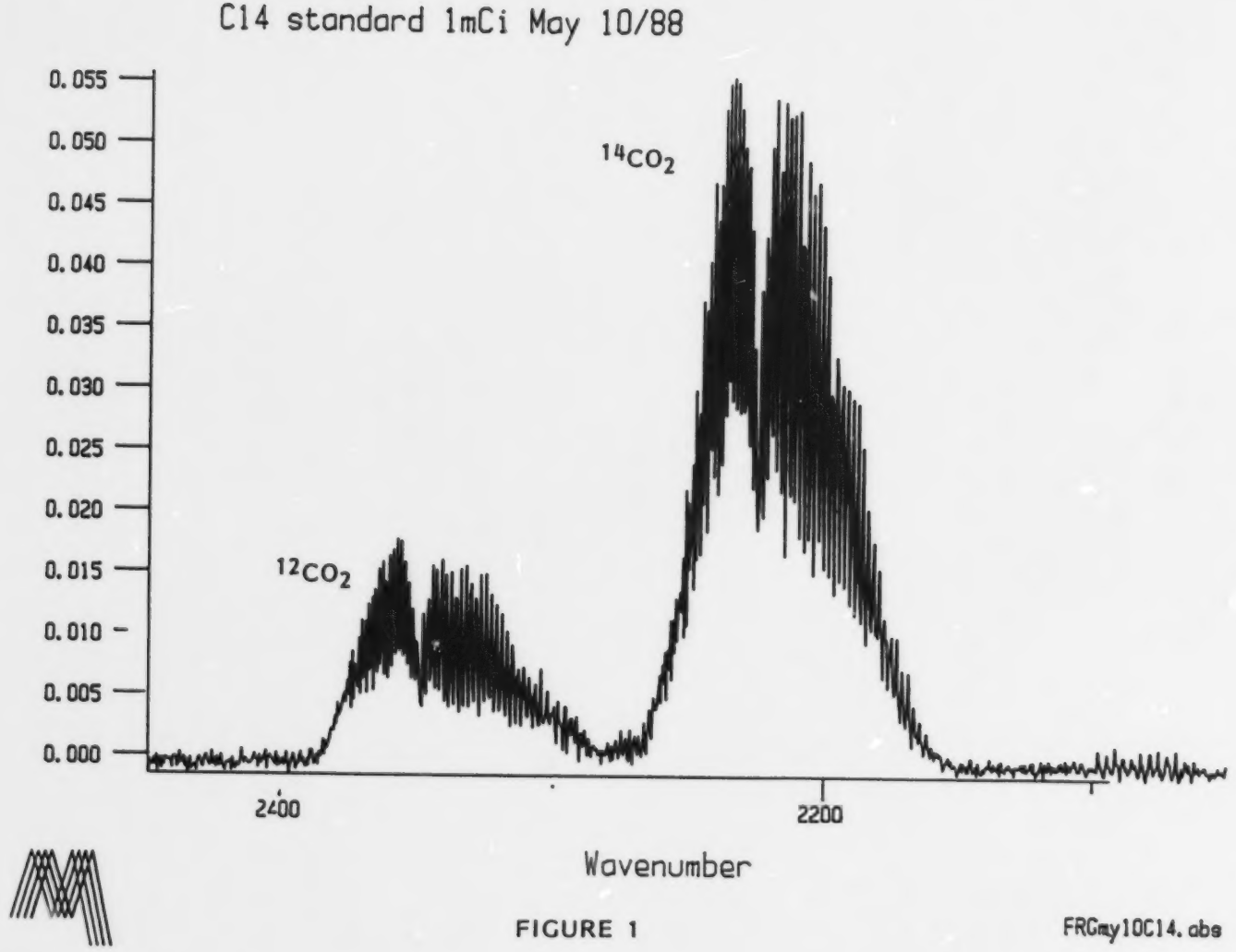


FIGURE 1

FRCmy10C14.abs

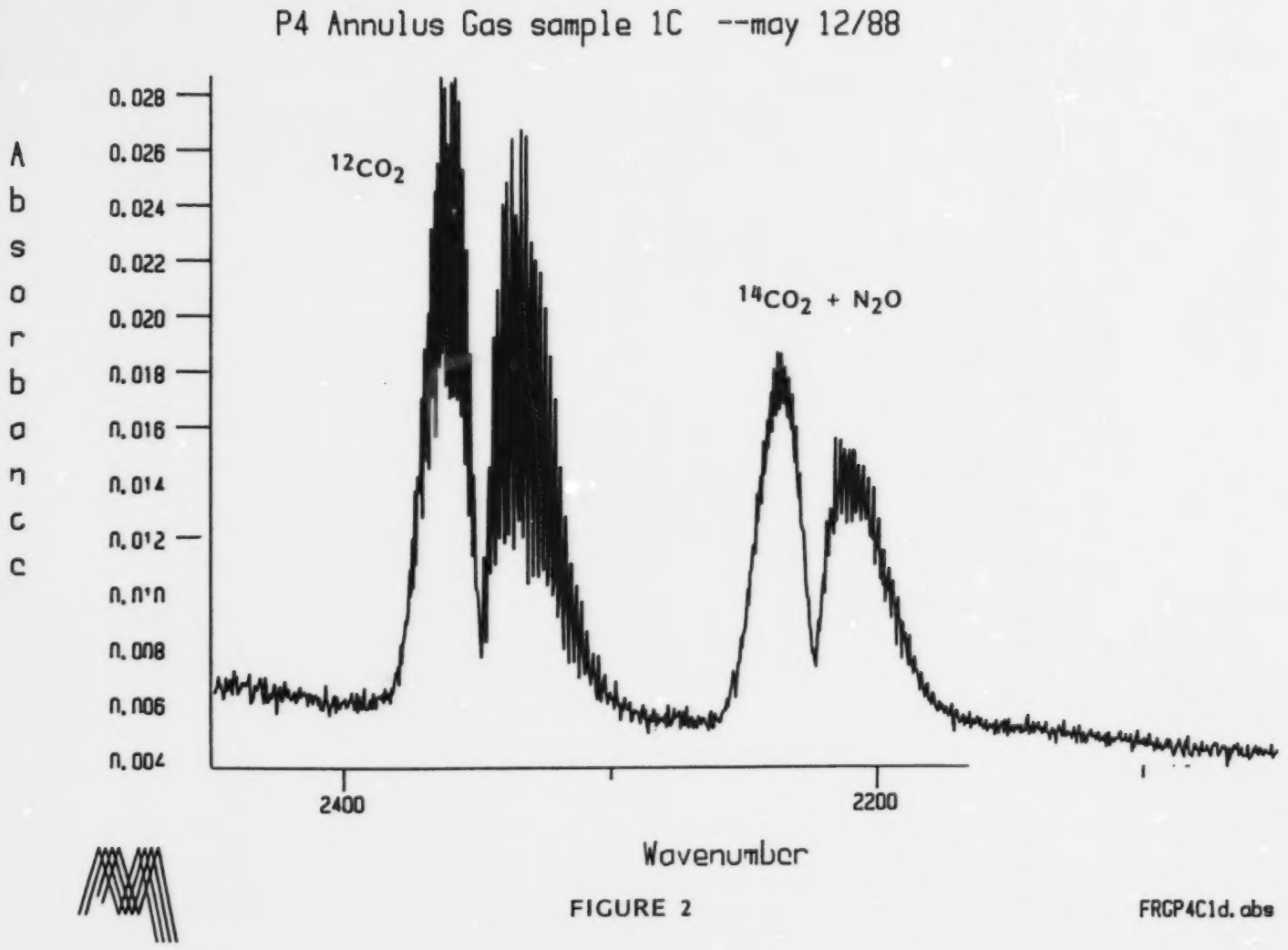


FIGURE 2

FRGP4C1d.abs

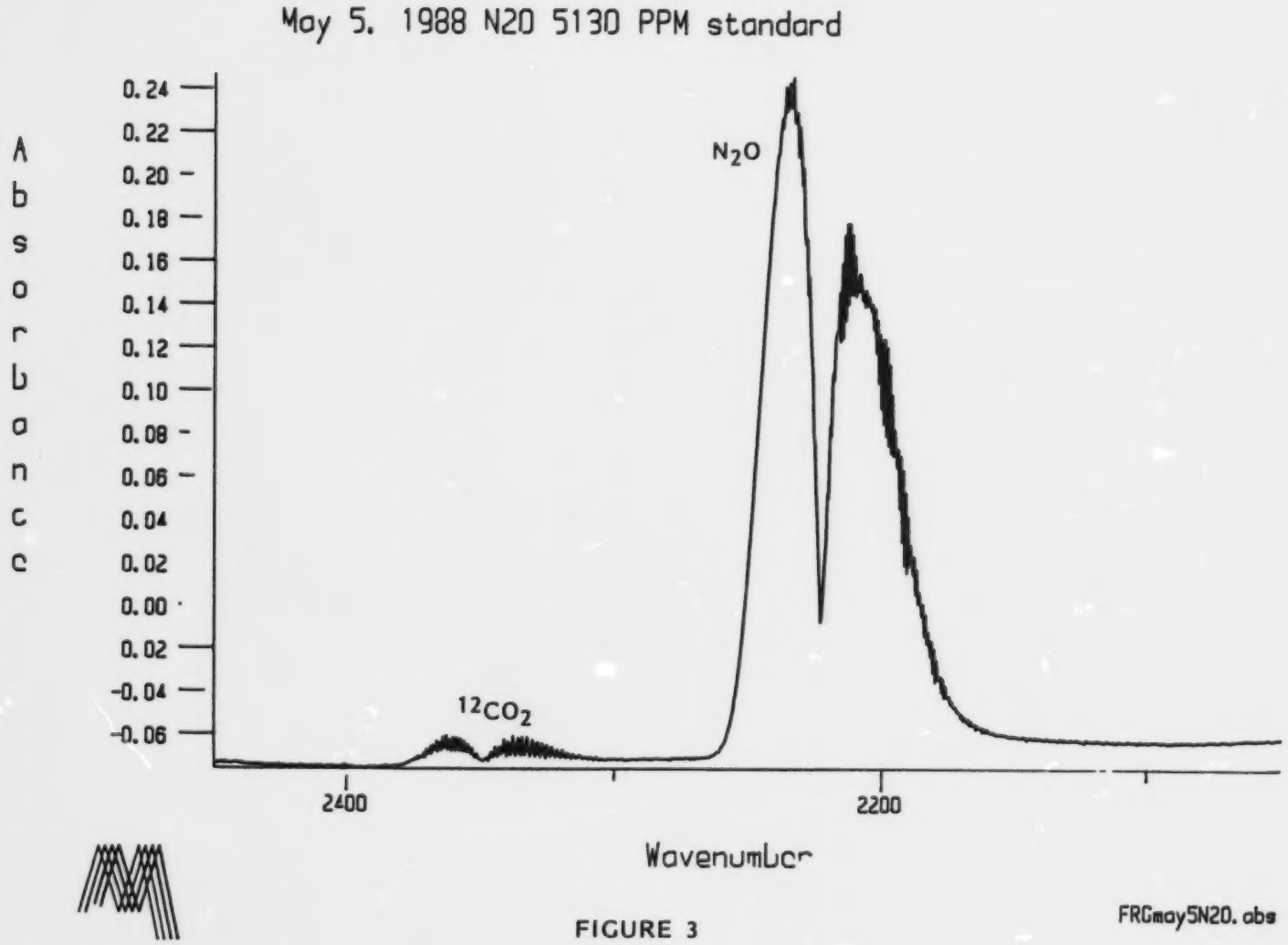
May 5. 1988 N20 5130 PPM standard
Absorbance
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.02
-0.04
-0.06
$N_2O$
$^{12}CO_2$
2400
2200
Wavenumber
FRGmay5N20.abs

FIGURE 3

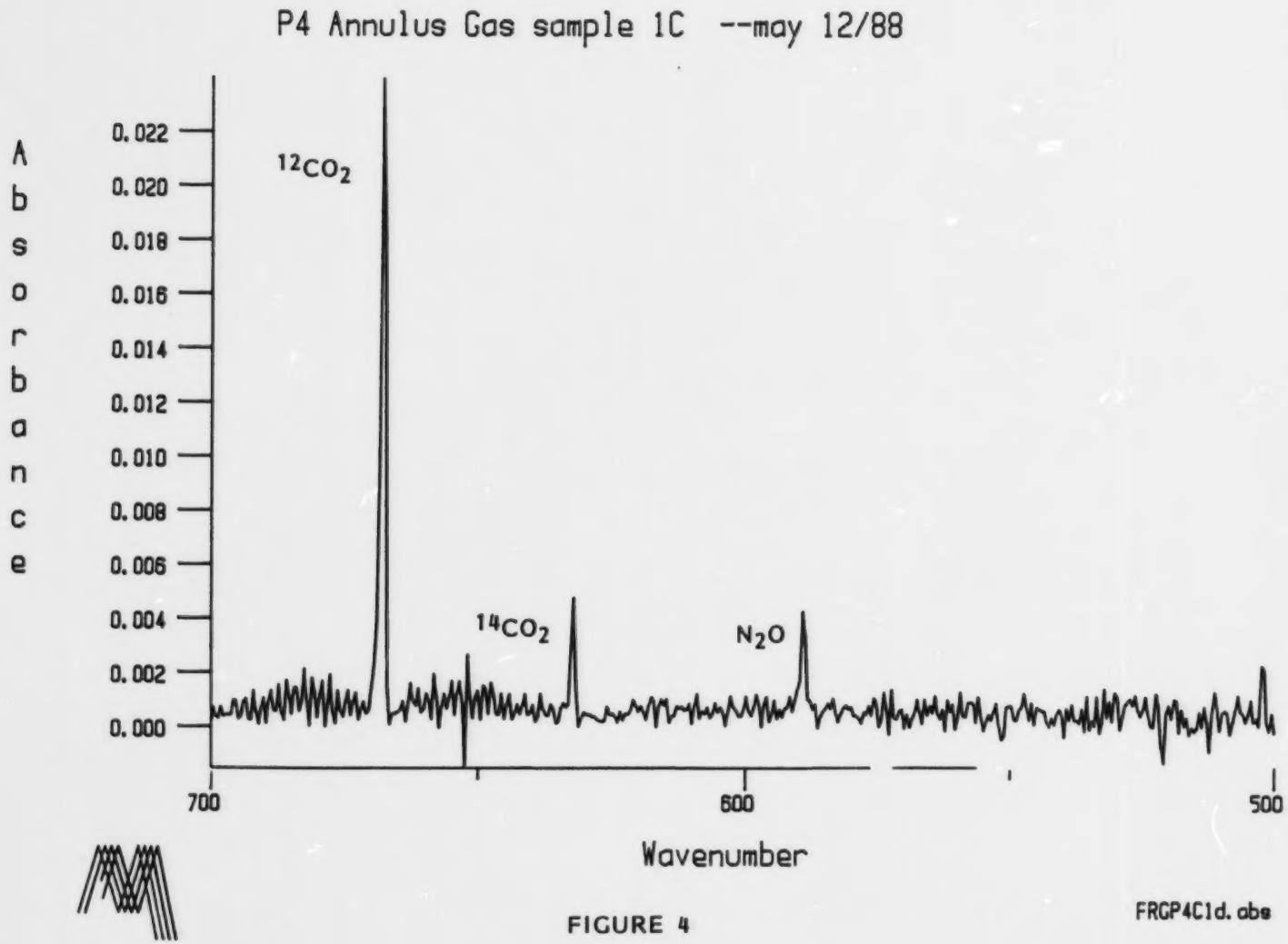
P4 Annulus Gas sample 1C --may 12/88
Absorbance
0.022
0.020
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
$^{12}CO_2$
$^{14}CO_2$
$N_2O$
700
600
500
Wavenumber
FRGP4C1d.abs

FIGURE 4

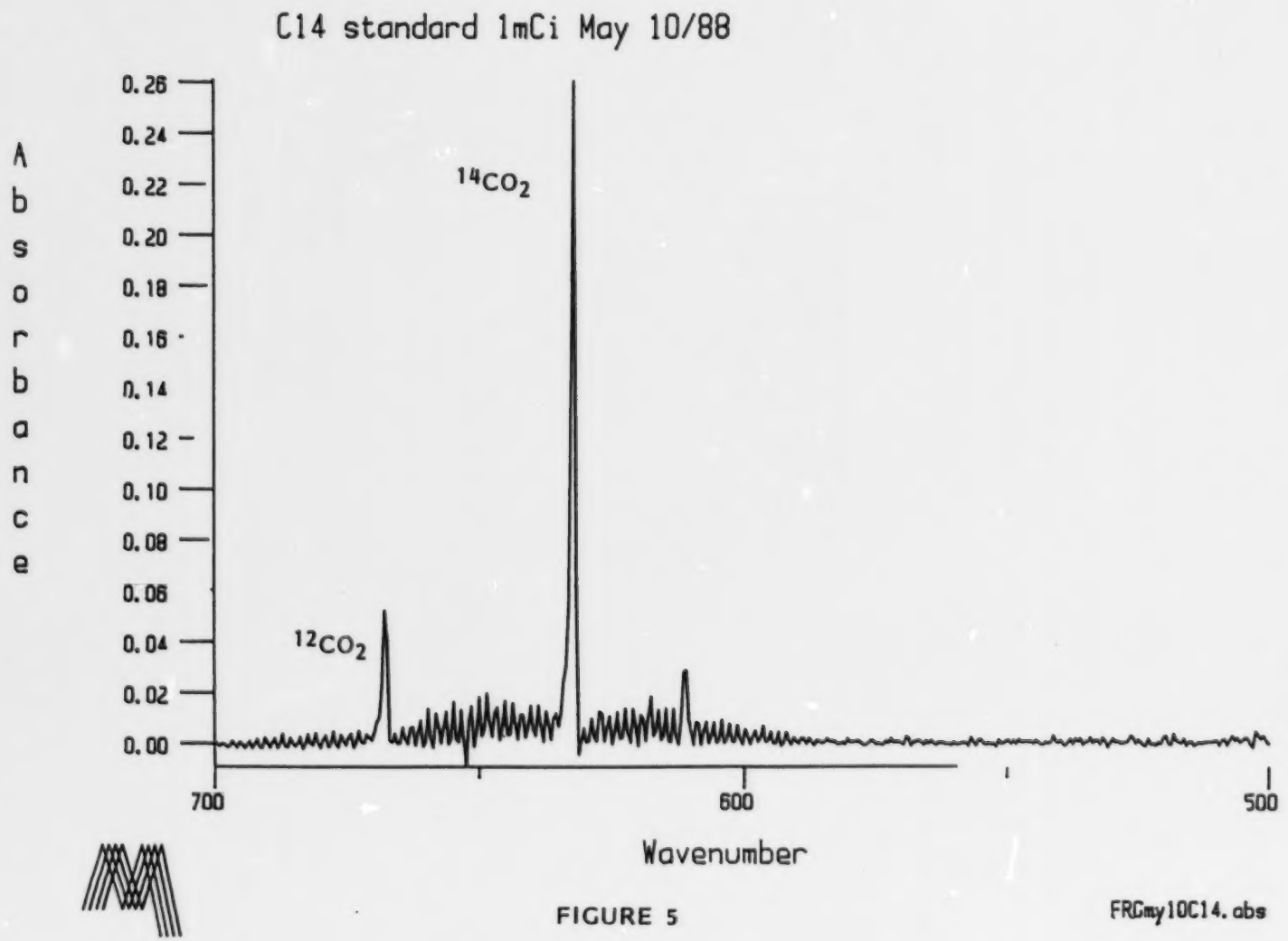


FIGURE 5

FRCmy10C14.abs

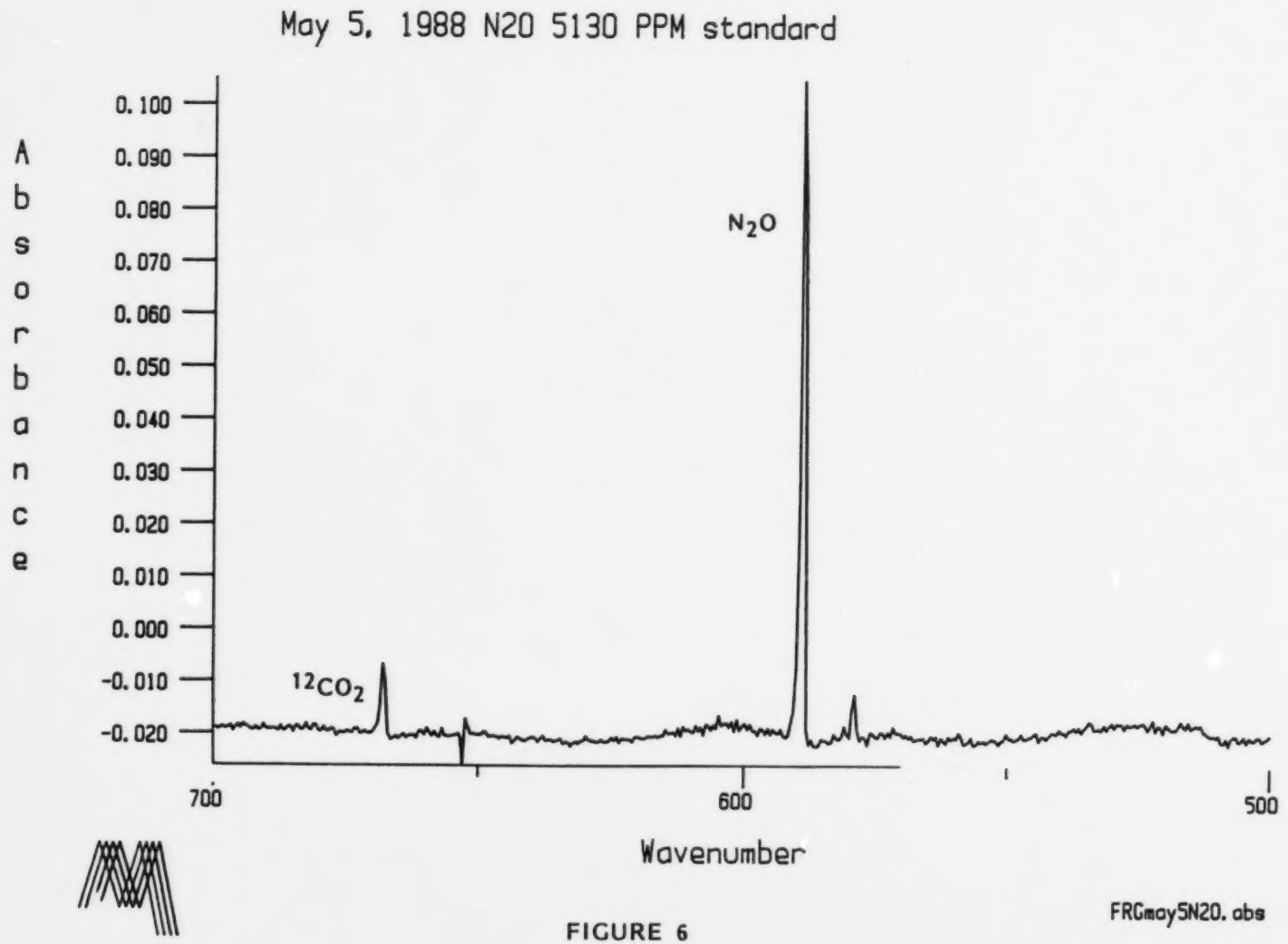
May 5, 1988 N20 5130 PPM standard
Absorbance
0.100
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
-0.010
-0.020
$N_2O$
$^{12}CO_2$
700
600
500
Wavenumber
FRGmay5N20.abs

FIGURE 6